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CHLORINATED AND NONCHLORINATED
ORGANICS STORAGE STUDIES

R. A. C. PROJECT NO. 412C
FINAL REPORT



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R. A. C. PROJECT NO. 412C
FINAL REPORT

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ABSTRACT

The widespread implementation of programs to monitor and control trace organic contaminants has brought with it a need to refine sampling, storage and analysis protocols. Of key concern is the stability of the compounds of interest in various sample types during transport and storage prior to analysis. This information would be of value, both in developing valid sampling and analysis procedures and in planning monitoring programs. The objective of this study was to compile information from existing sources regarding the stability of a variety of sample matrix/organic compound class combinations to recommend optimum sample storage conditions where possible, and to evaluate the completeness of the information available.

Sample matrices studied were air-cartridge (AIR-C), air-sorbent traps (AIR-S), air-filters (AIR-F), biota (BIO), drinking/surface water (DW), sediment (SED), vegetation (VEG), and waste waters (WW). Organic compound classes studied were acid extractable-phenolic (AE), base neutral extractable compounds (BN), carbamate pesticides (CP), chlorinated dibenzo-p-dioxins and dibenzofurans (DX), neutral chlorinated extractable (OC), organophosphorus pesticides (OP), acid extractable-phenoxy acid herbicides (PA), phenyl urea pesticides (PP), resin and fatty acids (RA), triazine herbicides (TR), volatile organics-halogenated (VH), volatile organics-non halogenated (VN), and volatile organics-sulphur compounds (VS). A listing of the compounds for each class is given in Appendix F.

Data was obtained from published stability studies. In some cases, information was extracted from other works which included sample stability aspects as a minor part. Unpublished sources of data were identified but very little of this information could be obtained.

Data obtained in the course of this study were compiled into a relational database. Storage recommendations were made after statistical analysis of this data. From Table 1, it can be seen that for some matrix/class combinations, the recommendations were made on limited data. For these combinations and for combinations where no data were obtained, recommendations for further experimental work were made. Methodologies for performing sample stability studies were examined with a view toward a standardized statistically validated approach in future work.

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1.0 INTRODUCTION

It is a truism that the quality of any decision is only as good as the information used in formulating it. In the case of laboratory analytical data, quality of information is a critical issue which depends on a wide range of factors beginning with sample collection and continuing throughout the process of sample storage, preservation, analysis, data handling, and reporting practices. This study addresses the stability during storage of environmental samples for trace organic analysis. Although several authoritative manuals (41, 74) provide extensive information regarding preservation and storage of samples for inorganic analysis, no comparable manual exists regarding samples for trace organic analysis. Toward this end, Enviroclean was engaged by the Ontario Ministry of the Environment to conduct a critical review of the literature and to make recommendations regarding storage times for which samples could be considered still valid for analysis.

1.1 Scope and Study Objectives

The primary purpose of this work was to assess the extent of information available regarding the stability during storage of approximately 350 trace organic contaminants in water (DW), waste water (WW), soil (SED), sediment (SED), air (AIR-C, AIR-F, AIR-S), vegetation (VEG), and biota (BIO). Specific objectives were:

- i) To collect and compile data from existing sources regarding the stability during storage of samples for each of thirteen compound classes in each sample matrix;
- ii) To critically evaluate the quality of data available for each compound class and matrix type;
- iii) Based on these data, to recommend maximum storage times for each compound class and matrix type;
- iv) To recommend areas for further research.

The following classes of compounds were evaluated:

<u>Compound Class</u>	<u>Code</u>
Neutral Chlorinated Extractables	OC
Volatile Organics - Sulphur Compounds	VS
Volatile Organics - Non-halogenated	VN
Volatile Organics - Halogenated	VH
Resin and Fatty Acids	RA
Chlorinated Dibenzo-p-dioxins and Dibenzofurans	DX
Carbamate Pesticides	CP
Phenyl Urea Pesticides	PP
Triazine Herbicides	TR
Organophosphorus Pesticides	OP
Base-neutral Extractable Compounds	BN
Acid Extractables - Phenolics	AE
Acid Extractables - Phenoxy Acid Herbicides	PA

A listing of the compounds for each class is given in appendix F.

1.2 Stability Studies

The availability of stability data is important to most if not all aspects of the analytical procedure. It is especially important in three areas; 1) scheduling and planning of field studies and subsequent analysis, 2) certification of standard and certified reference materials, and 3) specimen banking.

The scheduling and planning of field studies will depend on many factors including cost, objective(s) of study, stability of compounds of interest, transportation, scheduling and analysis. If the sample contains compounds that are stable for short periods of time then consideration as to transport and coordination with the analytical lab must be set up beforehand to ensure that analysis can be completed within the time period. On the other hand, if the compound is stable for longer periods of time, there will not be the same sense of urgency. Scheduling and coordination will still be needed but there is more leeway as to the completion of the analysis.

The use of stability data for reference materials is implied. The reference material usually contain instructions for storage and a past due date. This date, is the date past which the results obtained for the material can not be guaranteed. The data that was used to determine this date is usually not published but would be a useful source for the determination of stability if available.

The third area where stability data is being generated is in specimen banking. Specimen banks are being set up to store various samples for future analysis. The exact analysis to be performed may not be known or anticipated at the time of archiving. With slight modifications to the present procedure, a wealth of stability data can be produced. In addition to the storage of the specimens, spiked samples could be stored and analyzed at intervals to determine the long term stability of some compounds in various samples. What data that have been produced to date from studies with the specimen banks is not available or if available, is not extensive (224, 225, 226). It should be noted that the stability of the compounds to be analyzed for in these samples (at some future date) will have to be determined.

2.0 DATA COLLECTION

The data collection effort consisted of a computerized literature search combined with manual review of key handbooks and review documents, and personal contact with experts currently working in the field of analytical quality assurance and environmental specimen banking. Information obtained from these sources were compiled into a relational database using Dbase IV (Ashton-Tate, CA). From this, summary information was extracted for each compound class and matrix type to produce a series of information profiles from which storage recommendations were made.

2.1 Computerized Literature Search

The following databases were searched in the computerized literature survey:

- Chemical Abstracts
- NTIS
- Compendex
- Environmental Periodicals Bibliography
- Enviroline
- Pollution Abstracts
- Science Citation Index
- Water Resources Abstracts

The computerized search was used to identify existing scientific literature dealing specifically with sample storage and preservation. It was unknown at the outset whether such works would deal with only one or two compounds out of a class or with entire analytical groupings. Owing to the very large number of compounds within the scope of the survey, we elected as an initial search strategy to focus on sampling, sample storage, sample preservation, and synonyms of these terms as general keywords. A listing of keywords used in the computer searches can be found on page C-12 of Appendix C. This was found to be quite effective in producing a manageable number of citations as outlined in Appendices D and E. Copies of these citations will be included as a separately bound volume of this report.

Abstracts of the selected literature citations were printed, then manually reviewed to select those works most likely to contain relevant information. This produced a collection of approximately 320 papers which were obtained for detailed examination. These papers will be bound and included with the final report as separately bound volumes of this report.

2.2 Manual Search

Many aspects of the analysis of pesticides and herbicides in water, including sample storage and preservation were reviewed in detail in the handbook series edited by Chau and Afghan (227 - 229). Bibliographies of these works were manually reviewed to obtain further original citations dealing with sample storage and preservation.

A number of articles that were obtained were chosen subjectively (usually review articles or what seemed to be important papers in the field) for citation index searches. The result of these searches were examined and reviewed for works most likely to contain relevant information.

2.3 Contacts with Specialists

A key source of information for some compound classes and matrices was contact with research scientists working in various areas of environmental science. A list of individuals who provided data for use in this work is given in Appendix B. Among the agencies who provided data were:

Environment Canada - NWRI
Canadian Wildlife Service
Fisheries and Oceans Canada
National Research Council Canada
U.S. Environmental Protection Agency
Wisconsin Department of Natural Resources

2.4 Database Development

Because of the broad scope of the study and the need to compile and organize a very large amount of numerical data, a relational database using Dbase IV was developed. Information was organized into five files as follows:

<u>FILE NAME</u>	<u>DESCRIPTION</u>
BIBLIOG	Bibliographic information for each article examined. Each article was assigned an ascension number for referring to specific information taken from it.
CPD_LIST	The full list of compounds for which data was sought. For each compound the file contains the name, a unique alphabetical sorting key based on the compound name, the CAS Registry number, a two-letter code indicating the compound class, and selected physical constants for compounds for which data was readily available.

CLASSKEY	A listing of the compound classes with the corresponding class codes.
MATRIXKE	A listing of the sample matrices examined with their corresponding matrix codes.
CPD_DET	Detail records for each compound and storage condition for which data was obtained. Records in this file were linked to the Compound List through the CAS number, and to the Bibliography through the Ascension Number. Each record specified storage conditions, a storage time, and recovery for one compound.

Detailed listings of the file structures and the fields used for linking relationships between the various type of information are presented in Appendix C. To ensure accuracy in entry of the detailed information into the database, a short data entry program was written to perform the look-ups of ascension numbers and CAS numbers as the data was being entered. A listing of this program is also included in Appendix C.

Use of the relational database format greatly facilitated the process of compiling detailed numerical data from the papers reviewed. Articles were reviewed individually as they were received and the detailed information was added to the database on an on-going basis. Sorting and grouping the detailed data into summary tables was accomplished using a commercially available dbase report writer (R & R Report Writer, Concentric Data Systems, Bedford, MA). Articles used in this study are listed in numerical or ascension order and in alphabetical order in appendices D and E.

3.0 RESULTS AND DISCUSSION

In 1975, Thiers *et al* (62) wrote: "in clinical chemistry, [sample] stability is a critical consideration, but its assessment seems to have been neglected.". Upon review of approximately 320 articles covering a broad range of compound classes and sample matrices the same could also be said of trace organic analytical chemistry. Though the subject has been examined by a number of investigators, there is generally no consistent definition of stability. Experimental design rarely controls for variability in laboratory performance over time, the stability data reported was performed as an aside and not as the main thrust of the original study. Only a handful of the studies examined revealed a serious attempt to quantify the stability of samples for trace organic analysis during storage.

Measurement precision is a large practical problem in attempting to assess a change in a constituent concentration which might be attributable to instability during storage. Errors of this type arise from two primary sources: the intrinsic precision of the method of analysis at the concentration in question and the day-to-day variability in laboratory performance. As an operational definition, however, a constituent can be considered stable under specified storage conditions if it changes by less than one standard deviation at a 95 percent confidence level (62).

In many cases, there is a wealth of data available but in unpublished form. It is understood that the U.S. Fish and Wildlife Service has a large body of organochlorine pesticide data. We were unable to obtain this data as the authors would only release the data after publication. The National Institute of Standards and Technology (National Bureau of Standards) in the United States has a large body of stability data for many classes of organic pollutants. This body of data was used for determining the stability of standard reference materials. By deduction, any agency that markets certified reference materials should have stability data for the appropriate materials. Recommendations made in this report are based on the information on hand. Table 1 shows the number of data entries obtained for each matrix-compound class in this study. A summary of the recommendations made for each matrix-compound class are presented in table 2.

For most compound classes, there was no data available for the waste water matrix. In most cases, the definition of waste water is so broad that almost any water can be included in this matrix. For compound classes for which waste water data was obtained the difficulty arose from the different types of waste water used and whether it was treated or how it was treated. For future studies, the difficulty of obtaining a representative waste water will have to be addressed.

Table 1. Number of Data Points for
Sample Matrix–Organic
Compound Class Combinations

Compound Class	Matrix							
	AIR-C	AIR-F	AIR-S	BIO	DW	SED	VEG	WW
AE	0	0	0	* 24 *	937	0	0	0
BN	0	32	0	2	442	36	0	72
CP	XXX	XXX	XXX	XXX	8	10	38	0
DX	0	0	0	0	31	0	0	0
OC	4	0	0	264	844	14	14	11
OP	XXX	XXX	XXX	* 7 *	48	2	55	5
PA	XXX	XXX	XXX	XXX	9	2	2	0
PP	XXX	XXX	XXX	XXX	0	XXX	XXX	1
RA	XXX	XXX	XXX	XXX	0	XXX	XXX	64
TR	XXX	XXX	XXX	XXX	4	9	6	0
VH	67	0	0	XXX	158	18	XXX	2
VN	50	2	0	XXX	23	10	XXX	0
VS	0	0	0	XXX	XXX	XXX	XXX	XXX

* * – denotes combinations for which data was obtained
and reported but not required.

XXX – denotes combinations not required for this work.

3.1 Sampling and Sample Handling

While this aspect of the analysis process is not within the scope and objectives of this study, this is an important aspect to consider. If sampling and subsequent sample handling is suspect, then, the resulting values obtained will also be suspect. In this study, it is assumed that the correct sampling and sample handling techniques were used by the numerous researchers, unless otherwise noted. A case in point is the data obtained for volatile organics-non halogenated in the air-filter matrix where the samples were kept in an open container and losses to the atmosphere occurred.

3.2 Data Handling and Information Profiles

For compound class-matrix combinations where there is data available, statistical analyses (mean, standard deviation) of analyte recovery against temperature, concentration, preservative, and time were performed. For the cases where there was sufficient data, graphical representation of the data was produced. Analysis of stability data obtained resulted in recommendations as summarized in table 2. Recommendations were also made for cases where there was an accepted storage criteria. For the cases where there was stability data obtained, but not sufficient for realistic detailed statistical analysis, a more subjective criteria was used in addition to the statistical analysis. The result of this was a provisional recommendation. The provisional recommendation is based on limited data and more detailed studies and/or data will be needed for confirmation. For cases where no data was obtained and no existing criteria was found, a tentative recommendation was made based on common sense, behaviour of other compounds in the same matrix. These recommendations will have to be tested in more detailed stability studies.

Summaries of the data for the appropriate matrices and compound classes are presented in table 2. These summaries are the result of the analysis of the data in the database (given in appendix A) and comparison to accepted criteria (if available).

TABLE 2 - Summary of Recommendations for Storage

List of Abbreviations

AE	Acid Extractables - Phenolics
AIR-C	Air - Canister or Bag
AIR-F	Air - Filter
AIR-S	Air - Sorbent Trap
BIO	Biota
BN	Base-Neutral Extractable Compounds
CP	Carbamate Pesticides
DW	Drinking/Surface Water
DX	Chlorinated Dibenzo-p-dioxins and Dibenzofurans
OC	Neutral Chlorinated Extractables
OP	Organophosphorus Pesticides
PA	Acid Extractables - Phenoxy Acid Herbicides
PP	Phenyl Urea Pesticides
RA	Resin and Fatty Acids
SED	Sediment
TR	Triazine Herbicides
VEG	Vegetation
VH	Volatile Organics - Halogenated
VN	Volatile Organics - Non-Halogenated
VS	Volatile Organics - Sulphur Compounds
WW	Waste Water

TABLE 2 - continued

Compound Class
Acid Extractables - Phenolics (AE)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	Tentative recommendation - store SUMMA canisters or glass sample containers at 25°C for up to 12 days before analysis.
AIR-F	Tentative recommendation - store filters at -20°C under air-argon gas mixture. Samples are stable for at least 2 years.
AIR-S	Tentative recommendation - follow U.S. E.P.A. protocol of sampling with distributed air volume sets. Sample tubes are sealed; refrigerated; analysis to be completed between 7 and 30 days after sampling.
BIO	Provisional recommendation - store at -20°C for up to 15 weeks with no preservation.
DW	Preserve with chloroform, stable for 3 weeks except for pentachlorophenol and some tetrachlorophenol. In this case use 5 ug/L H ₂ SO ₄ but some losses may occur for all compounds.
SED	Tentative recommendation - store at -20°C for up to 15 weeks with no preservation.
VEG	Tentative recommendation - store at -20°C for up to 15 weeks with no preservation.
WW	Tentative recommendation - follow recommendation for drinking water or U.S. EPA protocol of collection in an amber glass container with teflon lined cap; add 0.008% Na ₂ S ₂ O ₃ if chlorine presence is known or suspected; refrigerate; extract within 7 days and analyze within 40 days of extraction.

N/A - Not Applicable

Table 2 - continued

Compound Class
Base-Neutral Extractable Compounds (BN)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	Tentative recommendation - store SUMMA canisters or glass sample containers at 25°C for up to 12 days before analysis.
AIR-F	Provisional recommendation - store filters at -20°C under air-argon gas mixture. Samples are stable for at least 2 years.
AIR-S	Tentative recommendation - follow U.S. E.P.A. protocol of sampling with distributed air volume sets. Sample tubes are sealed; refrigerated; analysis to be completed between 7 and 30 days after sampling.
BIO	Tentative recommendation - Extract on to glass fibre filters, store at -20°C under air-argon gas mixture. Samples are stable for at least 2 years.
DW	Preserve samples at pH 2 without chlorine; store at 4°C for up to 33 days before extraction and analysis.
SED	Provisional recommendation - store at -20°C for 3 days before extraction.
VEG	Tentative recommendation - store at -20°C for 3 days before extraction.
WW	Provisional recommendation - preservation with formaldehyde; storage at 4°C; analysis to be completed within 56 days.

N/A - Not Applicable

Table 2 - continued

Compound Class
Carbamate Pesticides (CP)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	N/A
AIR-F	N/A
AIR-S	N/A
BIO	N/A
DW	Tentative recommendation - Extract in toluene; store at 3°C for up to 2 months before analysis or follow U.S. EPA protocol of collection in an amber glass container with teflon lined cap, pH 5-9; refrigerate; extract within 7 days and analyze within 40 days of extraction.
SED	Tentative Recommendation - Storage at 10°C or lower for maximum of 12 weeks.
VEG	Provisional recommendation - store samples at 4°C; extract as soon as possible and complete analysis within 30 days.
WW	Tentative recommendation - Extract in toluene; store at 3°C for up to 2 months before analysis or follow U.S. EPA protocol of collection in an amber glass container with teflon lined cap, pH 5-9; refrigerate; extract within 7 days and analyze within 40 days of extraction.

N/A - Not Applicable

Table 2 - continued

Compound Class
Chlorinated Dibenzo-p-dioxins and Dibenzofurans (DX)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	Tentative recommendation - store SUMMA canisters or glass sample containers at 25°C for up to 12 days before analysis.
AIR-F	Tentative recommendation - store filters at -20°C under air-argon gas mixture. Samples are stable for at least 2 years.
AIR-S	Tentative recommendation - follow U.S. E.P.A. protocol of sampling with distributed air volume sets. Sample tubes are sealed; refrigerated; analysis to be completed between 7 and 30 days after sampling.
BIO	Tentative recommendation - seal and store samples at -20°C and complete analysis as soon as possible.
DW	Provisional recommendation - Follow U.S. EPA protocol of collection in an amber glass bottle with teflon cap, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ if chlorine present; refrigerate; extract within 7 days and analyze.
SED	Tentative recommendation - seal and store samples at -20°C and complete analysis as soon as possible.
VEG	Tentative recommendation - seal and store samples at -20°C and complete analysis as soon as possible.
WW	Tentative recommendation - Follow U.S. EPA protocol of collection in an amber glass bottle with teflon cap, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ if chlorine present; refrigerate; extract within 7 days and analyze.

N/A - Not Applicable

Table 2 - continued

Compound Class
Neutral Chlorinated Extractables (OC)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	Tentative recommendation - store SUMMA canisters or glass sample containers at 25°C for up to 12 days before analysis.
AIR-F	Tentative recommendation - store filters at -20°C under air-argon gas mixture. Samples are stable for at least 2 years.
AIR-S	Tentative recommendation - follow U.S. E.P.A. protocol of sampling with distributed air volume sets. Sample tubes are sealed; refrigerated; analysis to be completed between 7 and 30 days after sampling.
BIO	Store PCB's at -20°C with no preservation for at least one year before analysis. Other compounds, store at -40°C for 4 weeks with no preservation or freeze drying; storage at -40°C for up to 6 months.
DW	Store samples at 4°C with no preservation, extract within 6 weeks and analyze. For longer storage times, addition of chloroform will increase storage time to 15 weeks.
SED	Tentative recommendation - store in glass containers at -85°C for up to 2 years before analysis.
VEG	Tentative recommendation - store samples at 4°C with extraction as soon as possible after sampling. Extracts can be stored at 4°C for up to 8 weeks and in some cases for 5 years.
WW	Tentative recommendation - collection in amber glass bottles; addition of chloroform; refrigerate; extract within 7 days and analyze.
N/A - Not Applicable	

Table 2 - continued

Compound Class
Organophosphorus Pesticides (OP)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	N/A
AIR-F	N/A
AIR-S	N/A
BIO	Tentative recommendation - extract in 2-propanol and store at -17°C for up to 6 months for most compounds.
DW	Provisional recommendation - store samples at 4°C for up to 6 weeks with no preservation.
SED	Tentative recommendation - samples to be stored at -85°C for up to 40 months with no preservation.
VEG	Provisional recommendation - store samples at 4°C; extraction within 7 days; extracts stable for 8 weeks and in some cases 7 months at 4°C.
WW	Tentative recommendation - store samples at 4°C; extract with 7 days; store extracts at 4°C and analyze as soon as possible.

N/A - Not Applicable

Table 2 - continued

Compound Class
Acid Extractables - Phenoxy Acid Herbicides (PA)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	N/A
AIR-F	N/A
AIR-S	N/A
BIO	N/A
DW	Tentative recommendation - collect samples in amber glass bottles; pH=2 with H ₂ SO ₄ ; samples stable for 50 days at 4°C.
SED	Tentative recommendation - store at -15°C for up to 33 days with no preservation before analysis.
VEG	Tentative recommendation - store unpreserved samples at -20°C for up to 73 weeks before analysis.
WW	Tentative recommendation - collect samples in amber glass bottles; pH=2 with H ₂ SO ₄ ; samples stable for 50 days at 4°C or follow U.S. EPA protocol of collection in amber glass bottle with teflon lined cap; pH 5-9, refrigerate; extract within 7 days and analyze within 40 days of extraction.

N/A - Not Applicable

Table 2 - continued

Compound Class
Phenyl Urea Pesticides (PP)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	N/A
AIR-F	N/A
AIR-S	N/A
BIO	N/A
DW	Tentative recommendation - follow U.S. EPA protocol of collection in an amber glass bottle with teflon cap; pH 5-9; refrigerate; extract within 7 days and analyze within 40 days of extraction.
SED	N/A
VEG	N/A
WW	Tentative recommendation - follow U.S. EPA protocol of collection in an amber glass bottle with teflon cap; pH 5-9; refrigerate; extract within 7 days and analyze within 40 days of extraction.

N/A - Not Applicable

Table 2 - continued

Compound Class
Resin and Fatty Acids (RA)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	N/A
AIR-F	N/A
AIR-S	N/A
BIO	N/A
DW	Tentative recommendation - preserve samples at pH 11; store at 3°C for up to 10 days before extraction and analysis.
SED	N/A
VEG	N/A
WW	Provisional recommendation - preserve samples at pH 11; store at 3°C for up to 10 days before extraction and analysis.

N/A - not applicable

Table 2 - continued

Compound Class
Triazine Herbicides (TR)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	N/A
AIR-F	N/A
AIR-S	N/A
BIO	N/A
DW	Tentative recommendation would be extraction of samples with ethyl acetate; storage at 24°C for up to 1 year in light or follow U.S. EPA protocol of collection in amber glass container with teflon lined cap; pH 5-9; refrigerate; extract within 7 days and analyze within 40 days of extraction.
SED	Tentative recommendation - dry at 45°C for 24 hours with analysis to be completed in 180 days. Store at -20°C.
VEG	Tentative recommendation - extract samples as soon as possible and complete analysis within 2 months. Store at 4°C.
WW	Tentative recommendation would be extraction of samples with ethyl acetate; storage at 24°C for up to 1 year in light or follow U.S. EPA protocol of collection in amber glass container with teflon lined cap; pH 5-9; refrigerate; extract within 7 days and analyze within 40 days of extraction.

N/A - Not Applicable

Table 2 - continued

Compound Class
Volatile Organics - Halogenated (VH)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	Tentative recommendation - store SUMMA canisters or glass sample containers at 25°C for up to 12 days before analysis.
AIR-F	Tentative recommendation - store filters at - 20°C under air-argon gas mixture. Samples are stable for at least 2 years or store sealed samples at 4°C for up to 6 days before analysis.
AIR-S	Tentative recommendation - follow U.S. E.P.A. protocol of sampling with distributed air volume sets. Sample tubes are sealed; refrigerated; analysis to be completed between 7 and 30 days after sampling.
BIO	N/A
DW	Follow U.S. EPA protocol of collection in an amber glass container with teflon lined septum; add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$; refrigerate; complete analysis within 14 days.
SED	Tentative recommendation - store samples at 4°C for up to 56 days before analysis with no preservation.
VEG	N/A
WW	Tentative recommendation - follow U.S. EPA protocol of collection in an amber glass container with teflon lined septum; add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$; refrigerate; complete analysis within 14 days.

N/A - Not Applicable

Table 2 - continued

Compound Class
Volatile Organics - Non-halogenated (VN)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	Tentative recommendation - store SUMMA canisters or glass sample containers at 25°C for up to 12 days before analysis.
AIR-F	Tentative recommendation - store filters at - 20°C under air-argon gas mixture. Samples are stable for at least 2 years or store sealed samples at 4°C for up to 6 days before analysis.
AIR-S	Tentative recommendation - follow U.S. E.P.A. protocol of sampling with distributed air volume sets. Sample tubes are sealed; refrigerated; analysis to be completed between 7 and 30 days after sampling.
BIO	N/A
DW	Provisional recommendation - store samples at 4°C for up to 56 days with no preservation before analysis or follow U.S EPA protocols of collection in amber glass bottle with teflon lined septum; 0.008% $\text{Na}_2\text{S}_2\text{O}_3$; refrigerate; analyze within 14 days.
SED	Tentative recommendation - store samples at 4°C with no preservation. Analysis to be completed within 56 days.
VEG	N/A
WW	Tentative recommendation - follow U.S EPA protocols of collection in amber glass bottle with teflon lined septum; 0.008% $\text{Na}_2\text{S}_2\text{O}_3$; refrigerate; analyze within 14 days.

N/A - Not Applicable

Table 2 - continued

Compound Class
Volatile Organics - Sulphur Compounds (VS)

<u>Matrix</u>	<u>Recommendation</u>
AIR-C	Tentative recommendation - store SUMMA canisters or glass sample containers at 25°C for up to 12 days before analysis.
AIR-F	Tentative recommendation - store filters at - 20°C under air-argon gas mixture. Samples are stable for at least 2 years or store sealed samples at 4°C for up to 6 days before analysis.
AIR-S	Tentative recommendation - follow U.S. E.P.A. protocol of sampling with distributed air volume sets. Sample tubes are sealed; refrigerated; analysis to be completed between 7 and 30 days after sampling.
BIO	N/A
DW	N/A
SED	N/A
VEG	N/A
WW	N/A

N/A - Not Applicable

3.2.1. Acid Extractables - Phenolics

No data was obtained in this study for the following matrices; air-canister, air-filter, air-sorbent trap, sediment, vegetation and waste water. There are no existing storage criteria for all the above mentioned matrices except for waste water.

For waste water, no data was obtained but the U.S. Environmental Protection Agency has a recommended storage criteria of; collection in an amber glass container with teflon lined cap; add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ if chlorine is present; refrigerate; extract within 7 days and analyze within 40 days of extraction.

Limited data (24) was obtained for biota. Provisional recommendations are to store at -20°C for up to 15 weeks with no preservation of sample. Even though there was no data obtained for the sediment and vegetation matrices, there are tenuous connections to biota, namely the possibility of bioactivity. The tentative recommendations for these two matrices would be to follow the same recommendation as for biota. A proper stability study would have to be performed before confirming this recommendation.

For drinking/surface waters, a large volume of data (937) was obtained. In this case it was possible to evaluate 5 different preservative conditions; chloroform, CuSO_4 , and H_2SO_4 under 4 different conditions. These are shown in figures A-1 to A-6. If pentachlorophenol or some of the tetrachlorophenols are not compounds of interest then the best form of preservation would be using chloroform. If however they are compounds of interest then preservation of the samples with between 5-50 $\mu\text{g/L}$ with H_2SO_4 is recommended. Losses of some of the compounds will occur. In all cases, storage of the samples will be at 4°C . Samples are stable for up to 15 weeks.

In the case of air-sorbent traps, no stability data was obtained. In work evaluated for this study, the U.S. EPA has a recommended procedure for sampling and storage. This procedure uses distributed air volume sets (324) which can readily identify if the data is good or if there are complicating factors present. It will not identify the complicating factor. For TENAX traps, the recommended procedure is to seal and refrigerate the tubes. Analysis to be completed within 7 to 30 days (323). This is a tentative recommendation for this matrix.

For the air canister matrix, a tentative recommendation for storage would be to follow the recommendation for this matrix as outlined for the volatile organics - halogenated or non-halogenated (sec 3.2.11 and 3.2.12). The samples are stored in SUMMA canisters or glass sample containers at 25°C for up to 12 days before analysis.

For air-filters, a tentative recommendation would be to follow the recommendation for this matrix as outlined in sec 3.2.2. or sec 3.2.12. These are extraction onto quartz glass fibre filters, store at -20°C under an air-argon matrix for up to 2 years (sec 3.2.2) or storage at 20°C with no preservation in sealed containers for up to 6 days before analysis (3.2.12).

3.2.2. Base Neutral Extractable Compounds

No data was obtained for the following matrices; air-canister, air-sorbent trap, and vegetation. For the air canister matrix, a tentative recommendation would be to follow the recommendation for the volatile organics - halogenated and non-halogenated (sec 3.2.11 and 3.2.12). This is storage of samples in SUMMA canisters or glass sample containers at 25°C for up to 12 days before analysis.

For the air-sorbent trap matrix, a tentative recommendation would be to follow the recommended U.S. EPA procedure as outlined above (sec 3.2.1.) and in references 323, 324 using distributed air volume sets.

For air-filters, a single paper (225) contained 32 entries for benzo[a]pyrene on glass fibre filters stored for up to four years. Samples were stable after two years with significantly higher recoveries at -20°C than at +20°C. There was no significant difference between filters stored under air and those stored under argon. The provisional recommendation for this compound-matrix combination is therefore to store for up to 2 years at -20°C. Storage under an inert atmosphere is not specifically indicated by the data but it would constitute prudent practice to avoid oxidation of labile compounds.

Only 2 entries were obtained for biota so storage recommendations were largely extrapolated from other related compound class-matrix combinations for which data were available. A provisional recommendation is therefore to extract within three days of collection and to store the extracts at -20°C for up to 2 years.

Thirty six entries were obtained for the sediment matrix, provisional recommendation is storage at -20°C for 3 days (see fig A-15). The use of preservatives should be investigated as data indicates that losses are apparent. No data was obtained for vegetation but as discussed in sec 3.2.1., the tentative recommendation would be to follow the recommendation as outlined for sediments.

For the waste water matrix, 72 entries were obtained. The data indicates (fig A-16, A-17) that a preliminary recommendation is preservation with formaldehyde, storage at 4°C, analysis to be completed within 56 days. This is contrary to the EPA criteria.

EPA criteria are collection in an amber glass container with teflon lined cap; add 0.003% $\text{Na}_2\text{S}_2\text{O}_3$; refrigerate; extract within 7 days and analyze within 40 days of extraction.

Four hundred and forty two entries were obtained for drinking water. Analysis of the data involved separating out the different preservatives, determining the mean recoveries and standard deviations. Graphical representation (fig A-9 to A-14) of this data indicates that the most favourable preservation technique is at pH 2 with no chlorine; store at 4°C for 33 days for most compounds (fig A-9). Reduced recoveries for some PAH's are evident for all the preservatives analyzed. No data was obtained for stability data with no preservatives. This possibility should be investigated as this is the recommended EPA sampling protocol.

3.2.3. Carbamate Pesticides

Limited data (8 entries) was obtained for drinking water and none for waste water. The data available is for one compound. Tentative recommendation is extract samples with toluene, store at 3°C for up to 2 months or use the U.S. EPA procedure of collection in an amber glass bottle with teflon lined cap, pH 5-9; refrigerate; extract within 7 days and analyze within 40 days of extraction. The same tentative recommendation is made for waste water matrix.

Ten entries were obtained for the sediment matrix. The number of compounds represented by this database is small. A tentative recommendation would be storage at 10°C or lower for a maximum of 12 weeks.

For the vegetable matrix, 38 entries were obtained but the number of compounds represented by these entries is small. Analysis of the data with no preservation (fig A-18) indicates that this is not the storage method of choice. The data indicated that some compounds can be stored for between 7 and 30 days or longer at low temperature (4°C) with no losses. The data indicates that the more stable form of storage would be as extracts as opposed to no preservation. Provisional recommendation is store samples at 4°C, extract as soon as possible and complete analysis within 30 days.

3.2.4. Chlorinated Dibenzo-p-dioxins and Dibenzofurans

No data was obtained for all matrices except drinking/surface water. For drinking/surface water, the data (31) obtained is limited. Analysis of the data with no preservation (fig A-10) reveals that this does not appear to be the long term storage method of choice. From the limited data obtained, the absence of chlorine is necessary, no preservation, and at 4°C would be ideal. This is consistent with the U.S. EPA sampling protocol of

no preservation. A tentative proposal would be the collection in an amber glass bottle with teflon cap, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ if chlorine presence known or suspected; refrigerate; extract within 14 days and analyze. For waste water matrices, bioactivity may be a factor, thus preservation at low pH may inhibit any activity. A tentative recommendation would be collection in an amber glass container with teflon cap; add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ if chlorine presence known or suspected; preserve at pH 2; refrigerate; extract within 14 days and analyze.

As dioxins and dibenzofurans are generally acknowledged to be stable, it would be reasonable to tentatively recommend that the same storage guidelines for air-canisters/volatile organic - halogenated combination (sec 3.2.11) be followed for dioxins.

For air-filters, storage of the filters at low temperature in a sealed container as for base neutral extractables (sec 3.2.2) can be tentatively recommended. For air-sorbent trap matrix, the tentative recommendation would be to follow the U.S. EPA protocol of using distributed air volume sets, sorbent traps to be sealed and refrigerated after collection, analysis to be completed between 7 and 30 days after collection.

In the case of biota, sediments, and vegetation, no data was obtained and using the fact that dioxins and dibenzofurans are relatively stable, a tentative recommendation would be to seal and store samples at -20°C ; extract and analyze as soon as possible after collection.

3.2.5. Neutral Chlorinated Extractables

No data was obtained for air-filter and air-sorbent trap matrices. Limited data was obtained for air-canister, sediment, vegetation and waste water matrices.

For the air-canister matrix, a total of 4 entries were obtained on 2 compounds. Due to the limited data, the tentative recommendation is store the sealed sample containers at ambient temperature, analyze within 7 days.

For air-filters, the tentative recommendation would be to store sealed sample containers under air-argon matrix at -85°C as outlined in sec 3.2.2. For air-sorbent trap matrix, the tentative recommendation would be to follow U.S. EPA practice of using distributed air volume sets as outlined in sec 3.2.1.

Sufficient data (264) was obtained for biota matrix, so that graphical representation was possible for some of the data (fig A-20 to A-24). Analysis of the data indicates that there are many possible storage techniques, however for some of the techniques, limited data was obtained and some of the techniques are not viable. Stability of pesticides in processed meat stored

in tin cans decreases over a period of 4 years. For the majority of matrices and compounds, a preliminary recommendation would be that PCB's are stable for at least 1 year after storage at -20°C with no preservation. For other compounds, storage at -40°C for 1 month with no preservation or freeze dry and store at -40°C for up to 6 months would be the recommendations. If some of the more volatile compounds are of interest then storage at -40°C with no preservation would be recommended. In this case, there may be some losses.

For drinking/surface water 844 entries were obtained. Graphical representation of the different concentrations of preservatives (fig A-25 to A-29) reveals that variations do exist for all of the methods. Analysis of the data indicates two methods to be superior; these are storage at 4°C with no preservation or preservation with chloroform. In the former case, the samples are stable for 6 weeks and 15 weeks for the latter case. The recommendation for this matrix/compound class combination would be storage at 4°C with no preservation; extract within 6 weeks of collection. If samples are to be stored longer then addition of chloroform is recommended.

Limited data (14) was obtained for the sediment matrix. Analysis of data indicates that storage at -85°C in glass containers for up to 24 months is feasible. This is the tentative recommendation for this matrix.

Fourteen entries were obtained for the vegetation matrix. Only 4 compounds from the target list are represented. Analysis of the data reveal that storage with no preservation is variable and that extracts are stable. Tentative recommendation is storage at 4°C with extraction as soon as possible after sampling. Extracts can be stored at 4°C for up to 8 weeks and in some cases for as long as 5 years.

Eleven data entries on a total of eleven compounds were obtained for waste water. The data obtained indicated variable recoveries at 4°C with no preservation for some compounds. Based on results obtained with drinking/surface water, tentative recommendation is collection in amber glass bottles; preserve with chloroform; refrigerate; extract within 7 days and analyze.

3.2.6. Organophosphorus Pesticides

Seven data entries were obtained for seven compounds for biota. A tentative recommendation is extraction in 2-propanol and storage at -17°C for up to 6 months for most target compounds. This matrix/compound class was not in the original scope of the project but has been included as data was obtained.

For drinking/surface water matrix 48 entries were obtained. Analysis of the limited data obtained indicates that extracts are

stable at 25°C for 6 weeks. The data also indicates that unpreserved samples stored at 4°C are also stable for 6 weeks. Provisional recommendation is storage of samples at 4°C for 6 weeks before extraction with no preservation.

A tentative recommendation for sediments would be storage at -95°C for up to 40 months. This is based on one observation each for two compounds on the target list. Even under these conditions, some losses are apparent.

A total of 55 entries were gathered for the vegetation matrix. Graphical representation (fig A-31) of recovery versus time for samples with no preservation indicates that this is not feasible. A comparison of these recoveries with those of extracts indicates that organophosphorus compounds are more stable upon extraction. Provisional recommendation is storage at 4°C; extraction of samples within 7 days; storage of extracts at 4°C for up to 8 weeks is possible and in some cases for as long as 7 months.

For waste water matrix 5 data entries were obtained. All data entries were for samples with no preservation. Recoveries indicate some form of preservation is necessary. Possible preservation methods are adjust pH to 2 or 10, chloroform or formaldehyde addition, extraction, etc. Based on the data for the drinking water matrix and as no information was obtained for addition of preservatives, a tentative recommendation is storage of samples at 4°C; extraction within 7 days. Extracts stored at 4°C for up to 8 weeks before analysis.

3.2.7. Acid Extractables - Phenoxy Acid Herbicides

Nine entries were obtained for drinking/surface water matrix. A total of 7 compounds are represented. Tentative recommendation is preservation of samples with sulphuric acid to pH 2 in an amber glass container. Storage of samples at 4°C up to 50 days before extraction and analysis.

One compound and 2 data entries were obtained for the sediment matrix. Tentative recommendation is storage at -15°C for up to 330 days with no preservation. The vegetation matrix also had 2 data entries for one compound. Based on limited data, tentative recommendation is storage of unpreserved samples at -20°C for up to 73 weeks.

No data was obtained for the waste water matrix in this study. Based on the data for drinking water, tentative recommendation would be preservation of samples with sulphuric acid to pH 2; storage at 4°C for up to 50 days before analysis or follow U.S. EPA protocol of collection in an amber glass bottle with teflon lined cap; pH 5-9; refrigerate; extract within 7 days and analyze within 40 days of extraction.

3.2.8. Phenyl Urea Pesticides

No data was obtained for drinking water matrix and 1 entry was obtained for waste water matrix. For the one entry, the analyte recovery was low after storage at 4°C for 4 weeks with no preservation. Tentative recommendation is to follow U.S. EPA protocol of collection in an amber glass container with teflon cap; pH 5-9; refrigerate; extract within 7 days and analyze within 40 days of extraction. This recommendation applies to both drinking and waste water matrices.

3.2.9. Resin and Fatty Acids

No data was obtained for drinking water matrix but 64 entries were obtained for waste water matrix. Analysis of the data, including graphical representation (fig A-32) of analyte recovery at pH 11 against temperature is sufficient to generate a provisional recommendation. Provisional recommendation for waste water matrix is preservation of samples at pH 11; store at 3°C for up to 10 days before analysis. This recommendation can be tentatively applied to drinking/surface water matrix.

3.2.10. Triazine Herbicides

Four data entries were obtained for drinking/surface water matrix and none for waste waters. Analysis of data obtained indicates that extraction of drinking/surface water samples with ethyl acetate; store at 24°C for up to 1 year in light or it may be appropriate to use U.S. EPA protocol of collection in amber glass container with teflon lined cap; pH 5-9; refrigerate; extract within 7 days and analyze within 40 days of extraction. These recommendations are tentatively applicable to both the drinking/surface and waste water matrices.

Limited data was obtained for sediments (9 entries for 2 compounds). Analysis of the data indicates a tentative recommendation of dry at 45°C for 24 hours with analysis to be completed within 180 days. Samples to be stored at -20°C.

Six entries for 2 compounds were obtained for vegetation. Analysis of data indicates that extraction of samples; storage of extracts at 4°C is stable for at least 3 weeks would be the tentative recommendation.

3.2.11. Volatile Organics - Halogenated

Sixty seven data entries were obtained for the air-canister matrix. Graphical representation of analyte recovery against time (fig A-33) and evaluation of the data indicates that storage in SUMMA canisters or glass sample containers at ambient air temperature (25°C?) is stable for 7 days within some exceptions (chloroform). The data indicates that some compounds are stable for 12 days. Provisional recommendation is to store samples in SUMMA canisters or glass containers at ambient air temperature with analysis to be completed within 7 days.

No data was obtained for air-filter or air-solvent trap matrices. For the air-filter matrix, tentative recommendation would be to follow the protocol as outlined in sec 3.2.12 for air filters and base neutral extractable compounds (sec 3.2.2). For air sorbent trap, tentative recommendation is to follow the U.S. EPA protocol using distributed air volume sets as outlined in sec 3.2.1. (323, 324).

For drinking water, 158 entries were obtained. Graphical representation of three different preservatives was possible (fig A-34 to A-37). Analysis of the data indicates that for the majority of compounds; no preservation, preservation with thiosulphate or ascorbic acid can be used. Of the three preservation methods, the use of thiosulphate would be the best choice, followed by ascorbic acid. Recommendations for this matrix would be to follow U.S. EPA protocols of collect in an amber glass bottle with teflon lined septum, preserve with 0.008% $\text{Na}_2\text{S}_2\text{O}_3$; refrigerate; complete analysis within 14 days.

For the sediment matrix, 18 entries were obtained for the sediment matrix. Analysis of the data indicates that tentative recommendations would be storage with no preservative at 4°C. Analysis to be completed within 56 days.

Two entries were obtained for waste waters. Storage was in open containers, losses to air occurred. Recoveries reported are suspect for this stability study. Tentative recommendation would be to follow U.S. EPA protocols of collection in an amber glass container with teflon lined septum; add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$; refrigerate and complete analysis within 14 days.

3.2.12. Volatile Organics - Non-Halogenated

Fifty Entries were obtained for the air-canister matrix. Graphical representation of the data is shown on fig A-38. Evaluation of the data indicate that preliminary recommendation would be to store sealed SUMMA canisters or glass sample containers at 25°C for up to 12 days before analysis.

Two entries for 1 compound (styrene) were obtained for the air-filter matrix. These results indicate that storage at 20°C for 6 days with no preservation is feasible. For obvious reasons, this is a very tentative recommendation. These results are very different for those reached for the base neutral extractable compounds and may not be applicable to other compounds in this compound class. The tentative recommendation is storage of sealed samples at 4°C for up to 6 days before analysis.

No data was obtained for air-sorbent trap matrix. Tentative recommendation is to follow U.S. EPA protocol using distributed air volume sets (sec 3.2.1., ref 323, 324).

For drinking water matrix, 23 data entries were obtained. Evaluation of the data indicates a provisional recommendation of store samples at 4°C for up to 56 days before analysis or follow U.S. EPA protocol of collection in an amber glass bottle with teflon lined septum; add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$; refrigerate; analyze within 14 days.

Ten entries were obtained for sediment matrix. Analysis of the data indicates a tentative recommendation of store samples at 4°C for up to 56 days before analysis.

No data was obtained for waste water matrix. Tentative recommendation for storage is to follow existing U.S. EPA protocol; collection of sample in an amber glass bottle with teflon lined septum; add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ if chlorine presence known or suspected; refrigerate; analysis to be completed within 14 days.

3.2.13. Volatile Organics - Sulphur Compounds.

No data was obtained for any of the matrices (air-canister, air-filters, air-sorbent trap) of interest. Tentative recommendations can be drawn from the behaviour of other compounds in the volatile organic classes (3.2.11, 3.2.12). These tentative recommendations are; for air-canister, store samples at 25°C in SUMMA canister or glass containers for up to 12 days before analysis; for air-filters, store sealed samples at 4°C for up to 6 days before analysis; for air-sorbent traps, follow U.S. EPA recommendations of using distributed air volume sets (ref 323, 324) as described in sec 3.2.1.

3.3 Conclusions

During the course of the study, little or no data could be obtained for the majority of matrices for each compound class. Tentative recommendations were made for matrix/compound class combinations in this category. For matrix/compound class combinations where limited data was obtained, provisional recommendations were the result. In cases where sufficient data

was gathered, recommendations were made and are valid for the compounds used in the analysis. The recommendations are most likely to be valid for the other compounds on the target list.

In some cases, the tentative or provisional recommendation are to use existing criteria. In these cases, supporting data for the criteria was not examined as it was not obtained from the source (usually U.S. EPA). In cases where the existing criteria conflicted with the data obtained, both recommendations were given. Only with more data can these recommendations be confirmed.

4.0 RECOMMENDATIONS AND FUTURE WORK

It is evident that there is a lack of good stability data. To fill in these gaps revealed by this study, planned stability studies should be initiated. The length of time for these studies will depend on the overall objectives of the study, the compound class and matrix in question. It would seem reasonable, to have the stability studies go for at least a week to a month if the objective was to prove the stability of the sample within the usual time needed to complete an analysis. If the objective was to determine the long term stability of extracts, then a 5 year storage time would not be unreasonable.

At all times, it is essential to minimize errors due to faulty sampling techniques or sample handling. A case in point is for biota. If the samples are to be frozen, the tissue will suffer moisture loss. These samples should be weighed into storage bottles, sealed, the weight recorded and then frozen. At the time of analysis, the entire sample should be used for analysis and the recorded weight used as the sample weight. Precautions such as this are necessary in order to prevent the inclusion of questionable or biased data.

Areas where there is a need for stability data, are identified in table 3. The priority for the performance of the individual studies is not addressed at this time. The priorities should be established by the Ministry in conjunction with their current regulations and workload. For some of the matrices (biota, sediment, and vegetation), special precautions have to be taken. Long term cold storage of these samples can result in weight losses. Corrections for this can be made if the original sample weight is taken at the beginning of the study before freezing. This weight can then used for all subsequent calculations of recoveries, etc (personal communication, K. Aspila, CCIW).

The experimental design of the stability study should follow the method suggested by Thiers et al. (62). The advantages of this method are 1) stability for any given condition can usually be determined within 15 data pairs; 2) experiment is ongoing, so lab resources are not tied down to just the stability study (a maximum of two samples for each study are analyzed each day for the duration of the study); 3) A statistical method can be applied to the determination of each compound; 4) Inter-run bias is minimized or cancelled depending on the study protocol; and 5) samples can be run as part of the regular analysis stream as long as experimental conditions remain the same.

Table 3. Sample Matrix-Organic
Compound Class Combinations
Requiring Stability Studies

Compound Class	Matrix							
	AIR-C	AIR-F	AIR-S	BIO	DW	SED	VEG	WW
AE	F	F	F	* C *	N	F	F	F
BN	F	F	F	F	N	C	F	C
CP	XXX	XXX	XXX	XXX	F	F	C	F
DX	F	F	F	F	C	F	F	F
OC	F	F	F	N	N	F	F	F
OP	XXX	XXX	XXX	* F *	C	F	C	F
PA	XXX	XXX	XXX	XXX	F	F	F	F
PP	XXX	XXX	XXX	XXX	F	XXX	XXX	F
RA	XXX	XXX	XXX	XXX	F	XXX	XXX	C
TR	XXX	XXX	XXX	XXX	F	F	F	F
VH	F	F	F	XXX	N	F	XXX	F
VN	F	F	F	XXX	C	F	XXX	F
VS	F	F	F	XXX	XXX	XXX	XXX	XXX

* * – denotes combinations for which data was obtained and reported but not required.

F – denotes a full study required

C – denotes a study for confirmation of recommendations

N – denotes no further study required

XXX – denotes combinations not required for this work.

Disadvantages to the method are 1) in order to cancel out inter-run bias, samples have to be run every day irregardless to holidays or weekends; 2) minimization of the inter-run bias can be achieved with a modification to the experimental design by choosing the days when the study will be performed which will increase the time of the study; 3) stability times that can be used are relatively short in order to keep the time of the stability study reasonable.

The experiment or study may not go as far as 15 data pairs. The study stops once a decision has been reached. This method has been verified in house for a variety of compounds. Usually the decision on stability is reached before 10 data pairs.

Parameters that have to be decided include preservative type (if any), storage time, storage temperature, sample container and target compounds.

With the increased popularity and proliferation of solid phase extraction (SPE) techniques for the extraction, storage and analysis of organic compounds in a variety of environmental matrices some effort should be made to document compound stability on solid phase extraction cartridges. SPE cartridges have the potential to be used as field sampling devices as well as in-laboratory analytical tools. Discussions with the Ministry regarding SPE use should identify potential study areas.

Recommended preservatives to be studied are none, chloroform, formaldehyde, pH 2, pH 7, and pH 10. Recommended temperatures to be studied are 4 and -20°C. All samples should be sealed in amber glass bottles to minimize degradation in light except for the air-canister matrix.

Certain matrix/compound classes have a higher priority, such as resin and fatty acids in drinking and waste water. This is due to the enacting of MISA regulations for the pulp and paper industry. Other matrix/compound class combinations may have the same or greater degree of urgency. Priorities can be more easily identified and set by the Ministry.

